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Alternative fuels for transportation vehicles: A technical review

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ABSTRACT

Recent petroleum crises, rapidly increasing its prices and uncertainties concerning petroleum availability threaten the sustainable development of the world economy. Both the environmental concern and availability of fuels greatly affect fuel trends for transportation vehicles. The present work aims to compile a holistic scenario of different resources, production technologies, and properties of alternative fuels for transportation vehicles. Detailed descriptions of production technologies and fuel properties would help to refine and further enhance the technologies. While many production technologies have been developed, still more attention is needed to develop an effective, economical and efficient conversion process. As a broad overview of the subject, this article includes information based on the research carried out globally by scientists according to their local socio-cultural and economic situations. The integration of different technologies and hybridization is the demand of the present time for sustainable power generation and economic development.

Contents

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1. Introduction

Increasing urbanization and industrialization have led to a phenomenal growth in transportation demand worldwide, coupled with a concentration of vehicles in metropolitan cities. The increasing power demand for industrialization and motorization of the world has led to a steep rise in the demand of petroleum-based fuels. The availability and environmental impact of energy resources will play a critical role in the progress of human beings and the physical future of our planet. At present, fossil fuels take nearly 80% of the primary energy consumed in the world, of which up to 58% alone are consumed by the transport sector [1–3].

1.1. Internal combustion engines and emissions

The internal combustion (IC) engines emit harmful pollutants like CO, CO_2, NOx, particulate matter, smoke, etc. Therefore, simultaneous power production and reduction in engine emissions are the most important research aspect in IC engines.

However, as engines are currently calibrated to be as efficient as possible while complying with the emission standards, there is still a trade-off between the emissions performance and efficiency. Among other solutions to reduce both NOx and PM such as reformed exhaust gas recirculation (REGR), selective catalytic reduction (SCR) catalysts and diesel particulate filters (DPF) are being used. But there is a major pollutant CO_2, which is a greenhouse gas also responsible for global warming, that remains the culprit.

The depletion of fossil fuels, rising petroleum prices and stringent environmental regulations have stimulated intense international interest in developing alternative non-petroleum fuels for internal combustion engines [4,5]. The utilization of non-petroleum based renewable alternative fuels like biofuels such as biodiesel, methanol, ethanol, dimethyl ether, diethyl ether, butanol, bioethanol, synthetic natural gas (SNG), Fischer–Tropsch diesels hydrogen etc. in the IC engines can be helpful to tame the CO_2 emissions. This is particularly desirable if those fuels can be employed successfully in existing engines with no modifications, or with minor modifications [3,6,7].

Subramanian et al. [8] presented the policy and planning issues for the utilization of ethanol and biodiesel in automotive diesel engines in Indian context in view of environmental benefits, energy self-sufficiency and boosting of the rural economy.

The biofuel is one of the options to fulfill the need as transport fuel. It received attention as environmental friendly renewable and substitute fuel. The biodiesel, which is an important biofuel, has been investigated worldwide for production, properties and sustainability aspect. The investigations are going on to employ biodiesel of well-known composition and purity and to report detailed analyses for utilization in diesel engine. The purity levels, which are necessary for achieving adequate engine endurance, compatibility with coatings and elastomers, cold flow properties, stability, and emission's performance must be better defined [9–11]. The second-generation fuels are the suitable alternative and viable fuels for the internal combustion engines [3].

The literature survey on alternative fuels have become a curtain riser, and the fact comes out that number of articles have been published on various fuels, covering the resources and production technologies, but hardly some work was found on alternative fuels in the collective form of information. The present paper is aimed at compiling the published information at the common platform, so that better and sustainable alternative fuels can be used for transportation vehicles, and further research can be enhanced for improvement and development.

2. Alternative fuels

The research on alternative fuels for transportation vehicles contributed a lot and many fuels like—biodiesel, methanol, ethanol, butanol, dimethyl ether, diethyl ether, bioethanol, synthetic natural gas (SNG), Fischer–Tropsch diesels hydrogen, straight vegetable oils (SVO), hydrotreated vegetable oil (HVO), synthetic natural gas (SNG), F-T diesel and hydrogen emerged as possible alternative fuels [12].

The ever increasing transportation vehicle density and fuel requirement compelled the researchers and the scientists to search for the alternative sources of the transportation fuels. Over the decades, many techniques and methods have been developed and still continue for betterment in terms of yield, cost economy and sustainability. The systematic study of the various sources of the alternative fuels and their production technologies is based on the fundamental principles of fuel design for internal combustion engine, as shown in Fig. 1.

Researchers have been re-directing their interests in biomass based fuels, which currently seem to be the only logical alternative

for sustainable development in the context of economical and environmental considerations. Renewable bio-resources are available globally in the form of residual agricultural biomass and wastes, which can be transformed into alternative fuels. Fig. 2 shows the classification of various biofuels [2] and Table 1 shows the alternative fuels, resources and present technology.

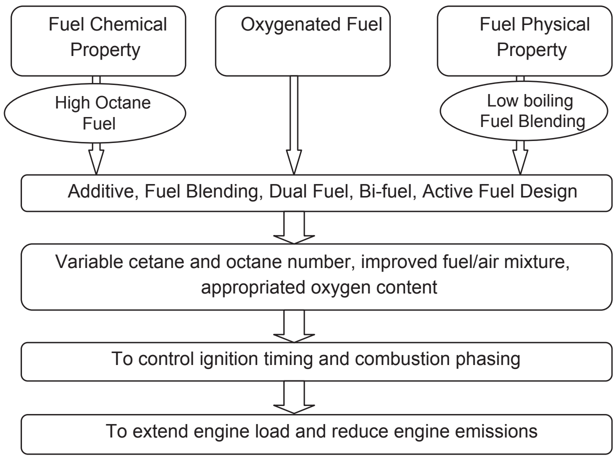


Fig. 1. Fundamental principles of fuel design for internal combustion engine [13].

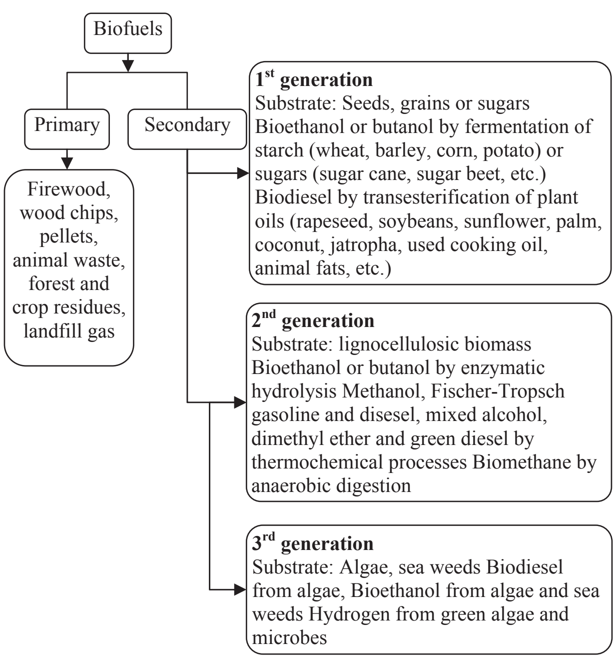


Fig. 2. Classification of biofuels [2].

2.1. Methanol

Methanol production involves the generation of syngas by steam reforming and water gas shift reaction. Synthetic natural gas (SNG) can be produced from wet biomass, coal etc. by hydrothermal gasification and thermo-chemical process [14]. Syngas can also be produced from fossil fuels, natural gas (NG), crude oil, coal, renewable resources: wood and municipal solid wastes etc. The syngas, then in the presence of copper oxide, zinc oxide, or chromium oxide-based catalysts and high temperature 800–1000 °C, yields methanol, as given by Eqs. (1)–(3), which represent the methanol synthesis.

Steam reforming reaction:

$$CH_4 + H_2O \xrightarrow[800\text{–}1000\,^{\circ}C,\ 20\text{–}30\ atm]{\text{Zinc based catalyst}} CO + H_2 \quad (1)$$

Water-gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

Methanol synthesis reaction:

$$2H_2 + CO \xrightarrow[800\text{–}1000\,^{\circ}C,\ 20\text{–}30\ atm]{\text{Zinc based catalyst}} CH_3OH \quad (3)$$

2.2. Ethanol

Ethanol is one of the biofuels having comparable fuel properties with diesel for internal combustion engines. Ethanol can be produced from molasses, sugar cane or starch, cereals, sugar beets, NG, shale oil, cellulosic biomass. First of all, the resource material is fermented, and then distilled up to the required purification. The chemical reaction of ethanol production is given by Eqs. (4) and (5). Besides the traditional process of ethanol production, over the period many other processes have been developed, which are shown in Fig. 3.

$$\overset{\text{Starch}}{(C_6H_{10}O_5)_n} + \overset{\text{Water}}{n(H_2O)} \rightarrow \overset{\text{Glucose}}{n(C_6H_{12}O_6)} \quad (4)$$

$$\overset{\text{Glucose}}{C_6H_{12}O_6} \overset{\text{Yeast}}{\Longrightarrow} \overset{\text{Ethanol}}{2(C_2H_5OH)} + 2CO_2 \quad (5)$$

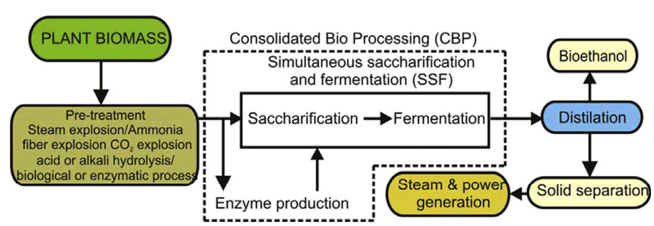


Fig. 3. Production of bioethanol from biomass [2].

Table 1
Alternative fuels, resources and present technology.

Fuel	Resources	Technology used	Reference
SNG	Wet biomass, Coal	Hydrothermal gasification Thermo-chemical process	[14,15]
Hydrogen	Coal char	Catalytic Coal gasification	[16]
Methanol	Natural Gas	Steam Methane Reforming Technology (SMRT)	[17]
Ethanol	Corn, Cassava	Fermentation and distillation	[17]
Butanol	Synthesis Gas	Fermentation—Butyribactarium Methelotrophicum	[18]
Bio-diesel	Seed oils, animal fats, the use of waste oils etc.	Transesterification	[12]
F-T Fuels	Coal, NG, Biomass	GTL Chemical conversion process	[19]
Dimethyl Ether (DME)	Methanol	De-hydrogenation of methanol Direct conversion from synthesis gas (Syngas)	[20]

2.3. Dimethyl ether

Dimethyl ether (DME) can be used as a clean high-efficiency compression ignition fuel with reduced NOx, SOx, and particulate matter. DME can be produced from natural gas, coal, biomass, etc. Hence, dimethyl ether production is not limited to one feedstock. It can be efficiently reformed to hydrogen at low temperatures, and does not have large issues with toxicity, production, infrastructure, and transportation as do various other fuels [21].

Song et al. [22] studied about the production of dimethyl ether (DME) from carbonaceous material, such as natural gas, coal, crude oil and biomass in the Republic of China. In China, the reserves of coal are abundant, accounting for 30% of the total quantity of the world reserve.

Traditionally, dimethyl ether has been produced in a two step process (i.e. the conventional route) where syngas (typically generated from the steam reforming of methane) is first converted to methanol—followed by methanol dehydration to dimethyl ether. The chemical conversion steps are shown by Eqs. (6)–(9) [20].

Methanol synthesis:

$$CO+2H_2 \leftrightarrow CH_3OH,\ \Delta H^{\circ}{}_{rxn}=-90.3\ \text{kJ mol}^{-1} \tag{6}$$

Methanol dehydration:

$$CH_3OH \leftrightarrow CH_3OCH_3+H_2O,\ \Delta H^{\circ}{}_{rxn}=23.4\ \text{kJ mol}^{-1} \tag{7}$$

Water-gas shift:

$$H_2O+CO \leftrightarrow H_2+CO_2,\ \Delta H^{\circ}{}_{rxn}=40.9\ \text{kJ mol}^{-1} \tag{8}$$

Net reaction:

$$3H_2+3CO \leftrightarrow CH_3OCH_3+CO_2,\ \Delta H^{\circ}{}_{rxn}=258.6\ \text{kJ mol}^{-1} \tag{9}$$

Developing DME from coal is of great importance for reducing vehicle dependence on petroleum fuels. The efficient technology of synthesizing DME from coal is under development and several pilot factories have been set up in China [22].

2.4. Butanol

In the series of alternative fuels, butanol is a very competitive renewable biofuel for use in internal combustion engines. The butanol production includes various methods for increasing fermentative butanol production, i.e. metabolic engineering of the Clostridia, advanced fermentation technique. The studies demonstrate that butanol, as a potential second generation biofuel, is a better alternative for the gasoline or diesel fuel, from the viewpoints of combustion characteristics, engine performance, and exhaust emissions. However, butanol has not been intensively studied when compared to ethanol or biodiesel, for which considerable numbers of reports are available.

Butanol (acetone, ethanol, and iso-propanol) are naturally formed by a number of clostridia. In addition, clostridia are rod-shaped, spore-forming Gram positive bacteria and typically strict anaerobes [23]. Jin et al. [24] studied a typical feature of the clostridial solvent production by biphasic fermentation. The first phase is the acidogenic phase, during which the acids forming pathways are activated, and acetate, butyrate, hydrogen, and carbondioxide are produced as major products. This acidogenic phase usually occurs during the exponential growth phase. The second phase is the solventogenic phase during which acids are reassimilated and used in the production of acetone, butanol and ethanol (or isopropanol instead of acetone in some *Clostridium beijerinckii* strains). The transition from acidogenic to solventogenic phase is the result of a dramatic change in gene expression pattern.

2.5. Biodiesel

The viable environmental friendly alternative fuel for compression ignition engines is methyl or ethyl esters (commonly known as biodiesel), which is derived from vegetable oils or animal fats [4]. The term biodiesel was originally used to describe unmodified vegetable oils that could substitute for diesel fuel (DF). Biodiesel is more suitable for compression ignition engines (Diesel Engines). Originally, the diesel engine was operated on vegetable oil. But later on there was an introduction of relatively cheap medium-weight diesel fuel which was used as fuel for transportation vehicles [25]. Since the 1930s, diesel engine has been fine-tuned to run on the diesel fraction of crude oil, which consists mainly of saturated hydrocarbons. As a result, modern diesel engines do not run satisfactorily on neat vegetable oils (NVOs) feedstock because of problems of high viscosity, deposit formation in the injection system and poor cold start [26].

The viscosity of vegetable oils should be reduced to prepare them suitably as fuels for internal combustion engines. Mainly, four techniques can be used to reduce the viscosity of vegetable oils; namely heating/pyrolysis, dilution/blending, micro-emulsion, and transesterification [27–29]. Biodiesel, a monoalkyl ester (methyl or ethyl ester) of long chain fatty acids derived from renewable lipid such as vegetable oils and animal fats, can be used as a substitution fuel for traditional diesel in any compression ignition (diesel) engines with little or no modification [30–32].

Biodiesel is a chemically modified alternative fuel for use in diesel engines, derived from vegetable oils and animal fats. Blending/dilution, microemulsification, thermal cracking and transesterification are the commonly adaptable methods to convert those vegetable oils as fuel in CI engine. Biodiesel is produced commercially by the transesterification of vegetable oils with alcohol. Methanol or ethanol is the commonly used alcohols, which can be produced from biomass sources, for this process [33]. Industrially, biodiesel (consisting of mixtures of a medium- to long-chain fatty acid alkyl esters, mainly methyl esters: FAMEs) is produced by relatively complex (catalytic) alcoholysis (transesterification) of vegetable oils and animal fats.

2.6. Biodiesel production

Biofuels can be produced from a variety of bio-feedstocks; they are renewable, sustainable, biodegradable, carbon neutral for the whole life cycle and environmentally friendly. They encourage green industries and agriculture and are applicable as motor fuels, without or with slight engine modifications. Several biofuels, including bioethanol, bio-methanol, biodiesel and bio-hydrogen, appear to be attractive options for the future of the transport sector. The production of biofuels is expected to rise steadily in the next few decades [34]. Biodiesel, namely fatty acid methyl esters (FAME), is an alternative diesel fuel [35,36]. The biodiesel production starts with the production of raw material (i.e. oil seed), which is mainly agricultural product or animal fat, through various phases that at last converts into biodiesel [10,37].

Biodiesel production is a modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages [38]. Depending on the alcohol used, biodiesel with different types of chemical composition is formed i.e. if methanol is used, methyl esters are formed, whereas with ethanol, ethyl esters are formed [2,39].

Kannan et al. [40] prepared Thevetia Peruviana Biodiesel (TPBD) in the laboratory using the seed oil of the plant. The 5 g of NaoH per litre of oil was mixed with 160 ml of methyl alcohol to produce methoxide. Oil was heated to 60 °C and the prepared methoxide then poured into the oil. The reaction was allowed for

one hour, and the final products were allowed to settle in the separating funnel overnight. Using distilled water, the biodiesel was washed four or five times to remove the impurities.

2.7. Ester preparation

2.7.1. Methyl esters

Canola methyl ester (CME), rapeseed methyl ester (RME), linseed methyl ester (LME) and sunflower methyl ester (SME) were synthesized in a batch type reactor using both potassium hydroxide (KOH) and sodium methoxide (CH_3ONa) as catalysts. The ester preparation involved a two-step transesterifcation reaction, followed by washing and drying. The two-step reaction utilized a 100% excess methanol, or a total molar ratio of methanol-to-oil of 6:1 with methanol equally divided in the two steps. 200 g of oil (about 0.22 mol) was placed in a dry flask equipped with a magnetic stirrer and thermometer. Dryness is absolutely essential as any water in the system will consume some of the catalyst and slow the transesterifcation reaction. In another flask, approximately 23 g of methanol was mixed with 1.0 g of KOH (i.e., 0.5% by the weight of oil), or 0.5 g of CH_3ONa, until all the catalysts dissolved. This mixture was quickly added to the oil and stirred vigorously for 20 min at 25 °C. After separation of glycerol in a separatory funnel, the top ester layer was poured into another flask and transesterified a second time using the same protocol as the first reaction. The crude ester was separated and washed with distilled water to remove the catalyst and unreacted methanol until it became completely translucent. Finally, the ester was dried with anhydrous sodium sulfate.

2.7.2. Ethyl esters

The ethyl esters of canola, rapeseed, linseed (flax) and sunflower oil (abbreviated as CEE, REE, LEE and SEE, respectively) were prepared in much the same way as the methyl esters but only using CH_3ONa catalyst. The transesterification was conducted at 70 °C (8 °C below the ethanol boiling point) for 2 h with vigorous agitation in order to achieve full conversion. As the ethyl esters tended to form emulsions with water, warm (50–60 °C) salt water was used as a substitute to reduce emulsification. Tannic acid in water (0.1% w/w) was also an effective washing solution. With mild agitation in a flask, the alcohol and most of the soap could be removed by three washes at 50 °C by either solution. After washing, the ethyl esters are dried over anhydrous sodium sulfate [41–43].

Minor edible oil crops like Argan oil, Tigernut, Cottonseed oil (CSO), Dark-coloured crude rice bran oil (CRBO), Corn oil, *Sesamum indicum* L (sesame), the Tea plant oil etc. are the various alternative edible oils that have suitable fatty acid compositions for use in biodiesel applications but are not expected to find large-scale application due to their high price and/or limited availability. The comparison of the different technologies to produce biodiesel is shown in Table 2.

2.8. Monitoring of transesterification reactions

The biodiesel is produced by transesterification in which, oil or fat is reacted with a monohydric alcohol in presence of a catalyst. The process of transesterification is affected by the mode of reaction condition, the molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature and purity of reactants. The technical tools and processes for monitoring the transesterification reactions like GCM, HPLC, GPCM and NIR can be summarized as follows [44].

2.8.1. Gas chromatographic method (GCM)

The glycerol, mono-, di-, and tri-glycerides can be analyzed on highly inert columns coated with apolar stationary phases without derivatization. The inertness of the column, required to obtain good peak shapes and satisfactory recovery, cannot be easily maintained in routine analysis. Trimethylsilylation of the free hydroxyl groups of glycerol, mono- and di-glycerides, however, ensures excellent peak shapes, good recoveries and low detection limits and enormously improves the ruggedness of the procedure. For complete silylation of glycerol and partial glycerides, the conditions of the derivatization reaction have to be controlled carefully. Extensive studies on the silylation of partial glycerides showed that silylation can be obtained under the following conditions; (i) bistrimethylsilyl trifluoroacetamide (BSTFA) as silylating agent, addition of pyridine or dimethyl formamide and heating to 70 °C for 15 min; (ii) BSTFAC 1% trimethylchlorosilane as silylating agent, addition of pyridine and a reaction time of 15 min at room temperature; (iii) N-methyl N-trimethylsilyl-trifluoroacetamide (MSTFA) as silylating agent, addition of pyridine and reaction time of 15 min at room temperature; (iv) MSTFA as silylating agent and heating to 70 °C for 15 min. The internal standard 1,2,4-butanetriol serves as a very sensitive indicator of incomplete derivatization [45].

2.8.2. High performance liquid chromatography method (HPLC)

A general advantage of HPLC compared to GC is that time and reagent consuming derivatization are not necessary, which reduces analysis time. The first literature on HPLC method describes the determination of overall content of mono-, di- and tri-glycerides in fatty acid methyl esters by isocratic liquid chromatography using a density detector. The separation was achieved by coupling a cyano-modified silica column with two GPC columns; chloroform with an ethanol content of 0.6% is used as an effluent. This system allowed for the detection of mono-, di- and tri-glycerides as well as methyl esters as classes of compounds. The system was useful for the study of degree of conversion of the transesterification reaction [46].

2.8.3. Gel permeation chromatography method

It is a method for simultaneous analysis of transesterification reaction products—monoglycerides, diglycerides, triglycerides, glycerol and methyl esters. The mobile phase was HPLC grade

Table 2
Comparison of the different technologies to produce biodiesel [38].

Variable	Alkali catalysis	Lipase catalysis	Supercritical alcohol	Acid catalysis
Reaction temperature (°C)	60–70	30–40	239–385	55–80
Free fatty acid in raw materials	Saponified products	Methyl esters	Esters	Easters
Water in raw material	Interference with reaction	No influence	–	Interference with reaction
Yield of methyl esters	Normal	Higher	Good	Normal
Recovery of glycol	Difficult	Easy	–	Difficult
Purification of methyl esters	Repeated washing	None	–	Repeated washing
Production cost of catalyst	Cheap	Relative expensive	Medium	Cheap

tetrahydrofuran at a flow rate of 0.5 ml/min at room temperature, and the sample injection size was 10 μL. Sample preparation involves only dilution and neutralization. For analysis, 300 mg of the sample was taken from transesterification reactor and neutralized by adding 5 ml HPLC grade tetrahydrofuran and one drop of 0.6 NHCl. The samples were then kept at 20 °C until analysis. Reproducibility of the method was good: analysis of palm oil transesterification products at different levels of conversion showed a relative standard deviation of 0.27–3.87%. Similarly GPC was used to evaluate the influence of different variables affecting the transesterification of rapeseed oil with anhydrous ethanol and sodium ethoxide as a catalyst. GPC has made the quantitation of ethyl esters, mono-, di- and tri-glycerides and glycerol possible [47,48].

2.8.4. NIR spectroscopy

The Near-infrared spectroscopy (NIRS) is a spectroscopic method that uses the near-infrared region of the electromagnetic spectrum (from about 800 nm to 2500 nm). Typical applications include pharmaceutical, medical diagnostics (including blood sugar and pulse oximetry), food and agrochemical quality control, and combustion research, as well as research in functional neuroimaging, sports medicine and science, elite sports training, ergonomics, rehabilitation, neonatal research, brain computer interface, urology (bladder contraction) and neurology (neurovascular coupling) [49]. NIR spectroscopy is used to monitor the transesterification reaction. The quantitation of the turn over from triglyceride feedstock to methyl ester product is based on the differences in the NIR spectra of these classes of compounds. At 6005 cm^{-1} and 4425–4430 cm^{-1}, the methyl esters display peaks, while triglycerides display only shoulders. Ethyl esters could be distinguished in a similar fashion. Using quantitation software, it is possible to develop a method for quantifying the turnover of triglycerides to methyl esters. The absorption at 6005 cm^{-1} gave the better results than the one at 4425 cm^{-1}. The mid range IR spectra of triglycerides and methyl esters of fatty acids are almost identical and offer no possibility for distinguishing. NIR spectra were obtained with the aid of a fiber-optic probe coupled to the spectrometer, which render their acquisition, particularly easy and time-efficient [50].

Many merits of biodiesel include being renewable energy resource, thereby relieving the reliance on petroleum fuel; and being biodegradable and non-toxic. Further, compared to petroleum-based diesel, biodiesel has a more favorable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons [51].

Use of biodiesel leads to many advantages such as providing green cover to the wasteland, support to agricultural and rural economy, and reduction independency on imported crude oil and reduction in air pollution [52].

2.9. Biodiesel from microalgae

Liquid fuel in the form of a mixture of hydrocarbons has been produced from a renewable form of biomass, the green Microalga Dunaliella, which is distributed in oceans and salt lakes throughout the world [53–57].

Miao and Wu [58] introduced an integrated method for the production of biodiesel from microalgae oil. Large amount of microalgae oil was efficiently extracted from these heterotrophic cells by using *n*-hexane. Biodiesel comparable to conventional diesel was obtained from heterotrophic microalgae oil by acidic transesterification. The best process combination was 100% catalyst quantity (based on oil weight) with 56:1 M ratio of methanol to oil at a temperature of 30 °C, which reduced product specific gravity from an initial value of 0.912 to a final value of 0.8637 in about 4 h of reaction time. The results suggested that the new process, which combined bioengineering and transesterification, was a feasible and effective method for the production of high quality biodiesel from microalgal oil.

The influence of catalyst quantity and temperature on the yield of biodiesel product at reaction conditions: 30:1 M ratio of methanol to oil, 160 rpm, 5 h of reaction time is shown in Fig. 4. The yield of biodiesel product with different molar ratios of methanol to oil at reaction conditions: 30 °C, 160 rpm, 100% catalyst quantity based on oil weight, 7 h of reaction time is shown in Fig. 5.

Sharma et al. [59] reported on advancements in development and characterization of biodiesel discussed about the effects of molar ratio, moisture and water content, reaction temperature, stirring, specific gravity, etc. on yield of biodiesel. Biodegradability, kinetics involved in the process of biodiesel production, and its stability have been critically reviewed. Emissions and performance of biodiesel have also been reported.

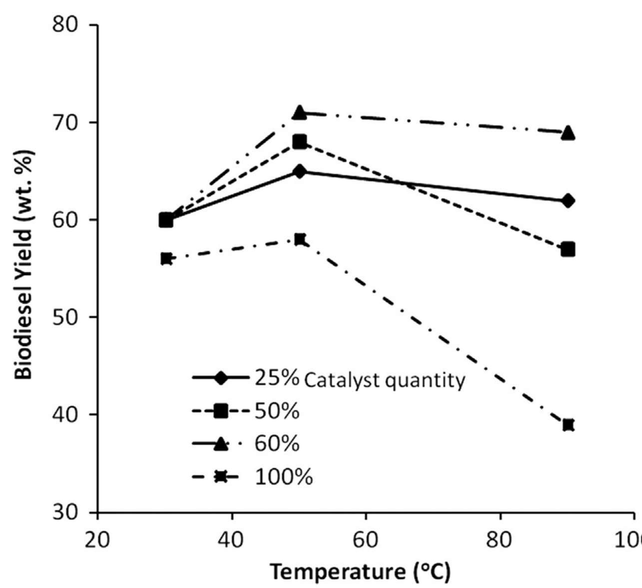


Fig. 4. The influence of catalyst quantity and temperature on the yield of biodiesel product. Reaction conditions: 30:1 M ratio of methanol to oil, 160 rpm, 5 h of reaction time [58].

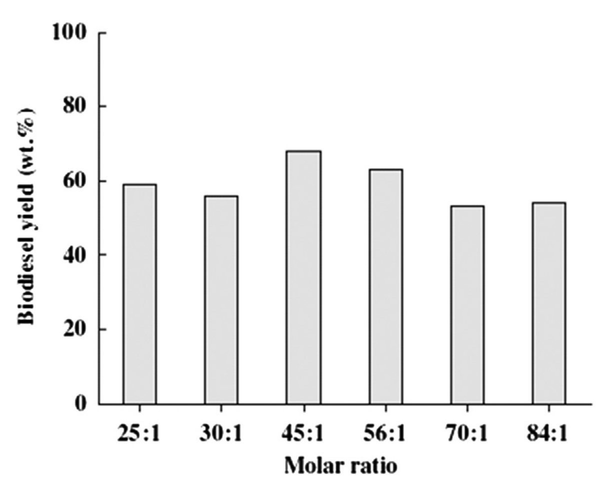


Fig. 5. The yield of biodiesel product with different molar ratios of methanol to oil. Reaction conditions: 30 °C, 160 rpm, 100% catalyst quantity based on oil weight, 7 h of reaction time [58].

Meng et al. [60] concluded that oleaginous microorganisms are available for substituting conventional oil in biodiesel production. Most of the oleaginous microorganisms like microalgae, bacillus, fungi and yeast are all available for biodiesel production. Regulation mechanism of oil accumulation in microorganism and approach of making microbial diesel economically competitive with petrodiesel are discussed in this review.

Diesel fuel can also be replaced by biodiesel made from vegetable oils. Biodiesel is now mainly being produced from soybean, rapeseed and palm oils. The higher heating values (HHVs) of biodiesels are relatively high. The HHVs of biodiesels (39–41 MJ/kg) are slightly lower than that of gasoline (46 MJ/kg), petrodiesel (43 MJ/kg) or petroleum (42 MJ/kg), but higher than coal (32–37 MJ/kg). Biodiesel has over double the price of petrodiesel. The major economic factor to consider for input costs of biodiesel production is the feedstock, which is about 80% of the total operating cost. The high price of biodiesel is in large part due to the high price of the feedstock. Economic benefits of a biodiesel industry would include value added to the feedstock, an increased number of rural manufacturing jobs, an increased income taxes and investments in plant and equipment. The production and utilization of biodiesel is facilitated firstly, through the agricultural policy of subsidizing the cultivation of non-food crops. Secondly, biodiesel is exempted from the oil tax. The European Union accounted for nearly 89% of all biodiesel production worldwide in 2005. By 2010, the United States is expected to become the world's largest single biodiesel market, accounting for roughly 18% of world biodiesel consumption, followed by Germany [37].

2.10. Bio-oil

Bio-oil is the state of technologies for second and third generation fuel production. First of all, raw biomass is converted in steps into crude pyro-oil and to a low calorific fuel substrates in gas, liquid or solid phase; then these substrates are catalytically converted to high grade fuels and hydrogen.

2.11. Pyrolysis

Pyrolysis is the thermal degradation of biomass by heat in the absence of oxygen, and results in the production of charcoal (solid), bio-oil (liquid), and fuel gaseous products. Pyrolysis of biomass has been studied for recovering a biofuel with medium to low calorific power. Depending on the operating conditions, pyrolysis can be divided into three subclasses: (i) conventional pyrolysis, (ii) intermediate/fast pyrolysis and (iii) flash pyrolysis.

Conventional pyrolysis occurs under a slow heating rate (0.1–1 K/s) and residence time is 45–550 s with massive pieces of wood as feedstock. The first stage of biomass decomposition (277–677 °C) is called pre-pyrolysis, which involves water elimination, bond breakage, appearance of free radicals, and formation of carbonyl, carboxyl and hydroperoxide group. Second stage of a solid decomposition proceeds with a high rate and leads to the formation of pyrolysis products. During the third stage, char decomposes at a very slow rate, and it forms carbon rich solid residues.

Intermediate pyrolysis occurs in high temperature range (300–700 °C), at a fast heating rate (10–200 °C/s), short solid residence time (0.5–10 s) and with fine particle (< 1 mm) feedstock. In the intermediate pyrolysis process, biomass decomposes to generate vapors, aerosol, and some charcoal like char. After cooling and condensation of vapors and aerosol, a dark brown mobile liquid (heating value, half of conventional fuel oil) is formed. Depending upon feedstock availability, intermediate pyrolysis produces: bio-oil, 60–75%, solid char, 15–25%, and non-condensed gases, 10–20%. Slow temperature and moderate residence time lead to pyrolysis liquid with low viscosity, low tar yield and high energy yield.

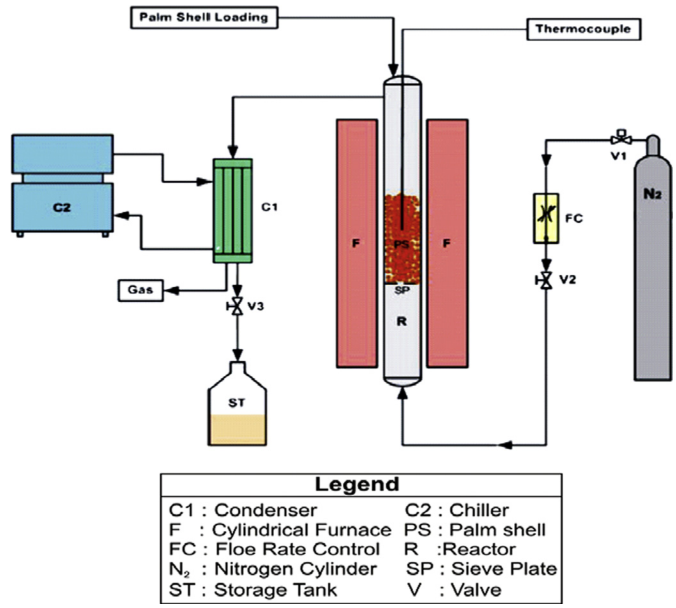


Fig. 6. Bio-oil production unit [63].

Flash pyrolysis occurs in very high temperature range (750–1000 °C), at a fast heating rate (> 1000 °C/s), short residence time (< 0.5 s) and with very fine particle (< 0.2 mm). Bio-oil production from biomass pyrolysis is typically carried out via flash pyrolysis and produced oil can be mixed with char to produce bioslurry, which can be easily fed to gasifier (pressure 26 bars, temperature 654–954 °C) for efficient conversion to syngas [61,62]. A bio-oil production unit is shown in Fig. 6 [63].

2.12. F-T Fuels

The Fischer–Tropsch (F–T) fuels are the synthetic fuels, generally known as gas-to-liquid (GTL) fuels. Franz Fischer and Hans Tropsch patented the chemical process of synthesis of petroleum at normal pressure using metal catalysts in 1926. The main interest in GTL is now in the Fischer–Tropsch synthesis of hydrocarbons. While synthesis gas (syngas) for GTL can be produced from any carbon-based feedstock, hydrocarbons, coal, petroleum coke, biomass, etc. and the lowest cost routes to syngas so far are based on natural gas.

Wilhelm et al. [64] in their study concluded that Fischer–Tropsch chemistry understandably is often regarded as the key technological component of schemes for converting synthesis gas or syngas to transportation fuels and other liquid products. However, syngas production itself accounts for more than half the capital investment and a disproportionate share of the operating costs for a GTL complex.

The F-T reaction produces hydrocarbons of variable chain length from a gas mixture of carbon monoxide and hydrogen. It is an exothermic reaction, as shown in Eq. (10). Tijmensen et al. [65] presented a basic schematic view of the key components for converting biomass to F-T liquids combined with gas turbine (combined cycle) power generation as shown in Fig. 7.

$$n\mathrm{CO} + (2n+1)\mathrm{H}_2 \rightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H}_2\mathrm{O}\ (\textit{Exothermic}) \quad (10)$$

Nowadays, F-T production process is operated commercially at Sasol South Africa (from coal-derived syngas) and Shell Malaysia (from natural gas-derived syngas). The main mechanism of the F-T reaction is shown in Eq. (11).

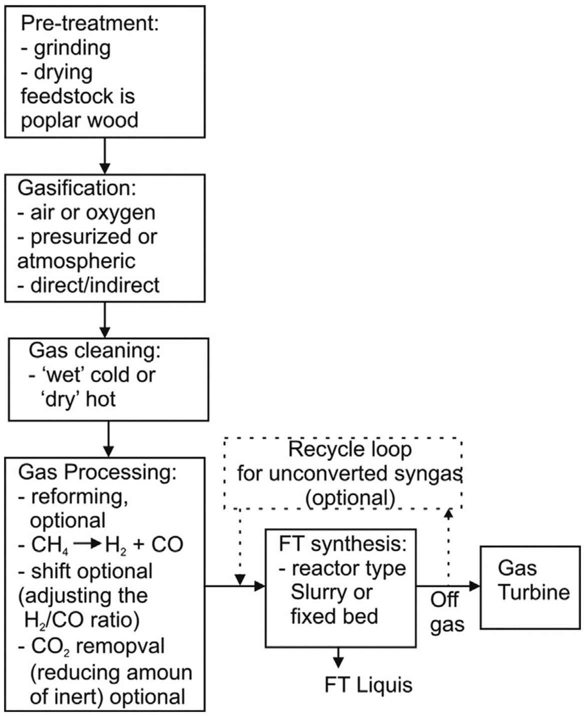


Fig. 7. A basic schematic view of the key components for converting biomass to F-T liquids combined with gas turbine (combined cycle) power generation [65].

$$CO{+}2H_2 \leftrightarrow {-}CH_2{-}{+}H_2O,\ \Delta H^\circ_{FT} = -165\ \text{kJ mol}^{-1} \quad (11)$$

The $-CH_2-$ is a building stone for longer hydrocarbons. A main characteristic regarding to the performance of the F-T synthesis is the liquid selectivity of the process. The liquid selectivity is determined by the so-called 'chain growth probability'. This is the chance that a hydrocarbon chain grows with another $-CH_2-$ group, instead of terminating [65–68].

Although the three processing steps that constitute the Fischer–Tropsch based Gas-to-Liquids (GTL) technology, namely syngas generation, syngas conversion and hydro-processing, are all commercially proven and individually optimized, their combined use is not widely applied.

Although the costs of large-scale commercial F–T plants have not yet been confirmed, but there is a good reason to believe that proposed and future GTL facilities will be substantially less costly than their very expensive predecessors. In a large measure, such cost reductions will be attributable to improvements in F–T catalyst and reactor design, the most significant of which have been pioneered by Sasol [3,69].

2.13. Hydrogen fuel

Globally, over 95% of hydrogen is produced from hydrocarbons, and about 4% is produced through electrolysis of water. Hydrogen is also produced as a by-product in chemical industries [70]. The hydrogen can be produced directly from fossil fuels and renewable energy sources, or indirectly from electricity via water electrolysis. There are several routes and other methods to produce hydrogen that are at different stages of research and demonstration. These methods include hydrogen production through the following:

- **Fossil fuels routes (Conventional processes)** are the processes in which fossil fuels are used as feed stock for the conversion process. The conventional processes include steam–methane reforming, thermal cracking of natural gas, thermal decomposition (i.e., partial oxidation) of heavy oil, catalytic decomposition of natural gas, coal gasification, steam–iron coal gasification etc.
- **Biomass and biological routes are** pyrolysis or gasification, which produces a mixture of gases (i.e., H_2, CH_4, CO_2, CO and N_2).
- **Water routes (non-hydrocarbon-based processes)** are electrolysis, photolysis, direct thermal decomposition or thermolysis, photochemical, photoelectrochemical and photobiological water splitting, biological hydrogen production, and integrated processes.
- **Electrolysis using renewable energy sources** are the processes of electrolysis with electricity produced from renewable energy sources; e.g. the combination of photovoltaics and electrolysis (PV–EL), the combination of wind power and electrolysis (W–EL) and the combination of hydropower and electrolysis (H–EL).

Integrated processes combine normally distinct technologies, using wastes from one process as feeds for another, to increase overall process efficiency [71].

The biological hydrogen production processes are found to be more environment friendly and less energy intensive, as they are mostly controlled by either photosynthetic or fermentative organisms [72].

Hydrogen in high purity can be produced through the electrolysis of water. The required electrical power can be supplied by renewable energy resources such as solar, wind, wave, tide or hydraulics, but electrolysis process is very slow and energy intensive, hence not sustainable in the present form [73].

2.13.1. Steam reforming

The steam reforming (SR) of hydrocarbons or alcohols with or without the presence of a catalyst produces hydrogen. The use of catalyst may result in quite low temperatures, short reaction times and liberate the maximum quantity of hydrogen held in water and the feed stock fuel [74].

The steam reforming process involves 'Steam reforming reaction', which combines water vapor and feed stock (i.e., natural gas, alcohols etc.) to produce hydrogen and carbon monoxide. The process includes mainly three stages, as shown in Fig. 8. Depending on the feedstock used, the SR processes can be classified as steam–methane reforming, steam–bioethanol reforming and steam–LNG reforming.

2.13.2. Steam–methane reforming

The steam–methane reforming (SMR) process for producing hydrogen from natural gas can be described in following steps [71]:

(1) *Reforming:* The methane feed is desulphurized and mixed with superheated steam. The endothermic reforming reaction, as shown by Eq. (12), occurs at 900 °C over a nickel-based catalyst in the reformer:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (12)$$

A raw synthesis gas exits at 370 °C and 3.5 MPa. Steam is produced in the boiler for compression and CO_2 stripping. The required process heat is supplied by combusting methane fuel:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (13)$$

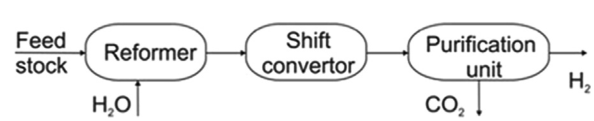


Fig. 8. Simplified process flow sheet for hydrogen production by steam reforming.

(2) *High-temperature shift:* Over a high-temperature catalyst in the shift converter, 94% of the CO in the raw gas is reacted via the exothermic water-gas shift reaction at 200–400 °C, as given in Eq. (14):

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (14)$$

The gas exits the high-temperature shift reactor at 220 °C, and preheats the incoming boiler and methanator feeds.

(3) *Low-temperature shift:* Over a low-temperature catalyst, 83% of remaining CO in the raw gas is reacted via the shift reaction. The gas exits the low-temperature shift reactor at 150 °C, and preheats incoming feed water.

(4) *Carbon dioxide removal.* The raw gas is compressed to 3.5 MPa using steam-turbine-driven centrifugal compressors. The primary diluent, CO_2, is removed in a scrubbing unit using the monoethanolamine process. The final CO_2 content of the raw gas is 0.1% by weight. Steam supplies the energy required by the CO_2 stripper (1910 kJ kg^{-1} CO_2 recovered).

(5) *Methanation:* Steam preheats the methanator feed to 350 °C and 2.4 MPa. Residual CO is converted in a methanator, where the exothermic methanation reaction occurs over a catalyst:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (15)$$

(6) *Cooling:* The hot product gas preheats feed water, and is cooled to 25 °C with cooling water. Water is separated and the product, containing 97% H_2 by weight, exits at 25 °C and 2.4 MPa. The main overall chemical reaction for SMR is given in Eq. (16):

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (16)$$

2.13.3. Steam bio-ethanol reforming

Production of hydrogen from bio-ethanol in the presence of nickel–copper bimetallic catalysts ($10Ni_5Cu/MgO/\gamma\text{-}Al_2O_3$) and steam is known as steam bio-ethanol reforming. Influential factors, such as reaction temperature, water-to-ethanol molar ratio, and liquid hourly space velocity (LHSV) affect the rate of hydrogen production. The conversions are always completed at temperatures above 400 °C, regardless of the changes of the reaction conditions. However, the yield to hydrogen increased with the increase in temperature and H_2O/C_2H_5OH molar ratio. The hydrogen yield up to 71% was reached under these conditions: 550 °C, LHSV of 5.0 h^{-1}, and H_2O/C_2H_5OH ratio of 10 over the $10Ni_5Cu/MgO/\gamma\text{-}Al_2O_3$ catalyst [75].

2.13.4. Thermal decomposition

In a thermal decomposition process, heat is added at suitable temperatures to dissociate the fuel. The thermal decomposition of hydrocarbon results in the formation of hydrogen and carbon, as shown in Eq. (17):

$$CH_{1.86} \rightarrow C_s + 0.93H_2 \quad (17)$$

In practice other hydrocarbon products are also formed, like methane, ethylene, etc., including aromatic compounds. The higher the temperature of decomposition, the more hydrogen the product gas contains. The difficulty of gasifying or handling the solid carbon makes hydrocarbon decomposition not suitable for onboard hydrogen generation [74].

2.13.5. Biomass-based hydrogen production methods

Biomass resources are the organic matters that consist of carbon, hydrogen, oxygen and nitrogen and comprise all the living matter (i.e., algae, trees and crops or animal manure etc.) present on the earth. Plants in presence of the solar energy, via photosynthesis, produce carbohydrates, which form the building blocks of biomass. Biomass can be converted into useful forms of energy products using a number of different processes. Various processes for conversion of biomass into hydrogen gas are comprehensively classified in two main groups, namely: Thermo-chemical conversion, and Bio-chemical/biological conversion [76].

2.13.5. (i) Thermo-chemical processes

Thermo-chemical conversion involves a series of cyclical chemical reaction for releasing hydrogen. There are mainly three methods for biomass-based hydrogen production such as pyrolysis, conventional gasification, and supercritical water gasification (SCWG).

Pyrolysis: It is a conversion of biomass to liquid, solid and gaseous fractions by heating the biomass in the absence of air at around 500 °C temperature. Pyrolysis may be defined as an incomplete thermal degradation of carbonaceous materials to char, condensable liquids (tar, oils or bio-oils) and non-condensable gases in the absence of air or oxygen. In addition to gaseous product, pyrolysis produces a liquid product called bio-oil, which is the basis of several processes for the development of the various energy fuels and chemicals. Pyrolysis reaction is an endothermic reaction. Fast pyrolysis is a thermal or thermo-catalytic conversion process, which can be characterized by rapid heating rates, quick quenching, and exclusion of oxygen from the reaction zone. It yields valuable chemical intermediates as well as synthesis gas from biomass.

There are three methods for producing hydrogen rich gas. Firstly, hydrogen can be produced by steam reforming of pyrolysis liquid obtained from the pyrolysis of biomass. Secondly, the pyrolysis process is carried out at high temperature around 700 °C in presence of catalysts normally dolomites and Ni, and includes the removal of tar content of the gas and improves the quality of the product gas. In the third option, pyrolysis occurs at a lower temperature (<750 °C) and catalyst is incorporated in the same reactor where the pyrolysis of biomass occurs.

Gasification: It is the conversion of biomass into a combustible gas mixture via the partial oxidation at high temperatures, typically varying from 800 to 900 °C. Although, the biomass could be converted completely to CO and H_2, some CO_2, water and other hydrocarbons, including methane in an ideal gasification, are also produced. The char compositions occurred by the fast pyrolysis of biomass can be gasified with gasifying agents (e.g., air, oxygen and steam) [76]. Reaction conditions along with heating values are mentioned as follows:

- Oxygen gasification: It yields a better quality gas of heating value of 10–15 MJ/Nm^3. In this process, the temperatures between 1000 and 1400 °C are achieved. O_2 supply may bring a simultaneous problem of cost and safety.
- Air gasification: A low heating value gas is produced containing up to 60% N_2 having typical heating values of 4–6 MJ/Nm^3 with by-products such as water, CO_2, hydrocarbons, tar, and nitrogen gas.
- Steam gasification: Biomass steam gasification converts carbonaceous material to permanent gases (H_2, CO, CO_2, CH_4 and light hydrocarbons), char and tar. This method has some troubles such as corrosion, poisoning of catalysts and minimizing tar components.

2.13.5. (ii) Biological conversion

The processes of biological hydrogen production can be broadly classified into two distinct groups. One is light dependent, and

the other is light-independent process. The biological conversion processes for hydrogen production include fermentative hydrogen production, photosynthesis process and hydrogen production by BWGS. All processes depend on hydrogen production enzymes.

There are three types of microorganisms of biohydrogen generation: cyanobacteria, anaerobic bacteria, and fermentative bacteria. The cyanobacteria directly decompose water to biohydrogen and oxygen in the presence of light energy by photosynthesis. Photosynthetic bacteria use organic substrates like organic acids. Anaerobic bacteria use organic substances as the sole source of electrons and energy, converting them into biohydrogen. Biological hydrogen can be generated from plants by biophotolysis of water using microalgae (green algae and cyanobacteria), fermentation of organic compounds, and photodecomposition of organic compounds by photo-synthetic bacteria [77].

Fermentative hydrogen production: Biohydrogen production is achieved by anaerobic (dark fermentation) and photoheterotrophic (light fermentation) microorganisms using carbohydrate rich biomass as a renewable resource. The first step is the acid or enzymatic hydrolysis of biomass to highly concentrated sugar solution, which is further fermented by anaerobic organisms to produce volatile fatty acids (VFA), hydrogen and CO_2. The organic acids are further fermented by the photo-heterotrophic bacteria (Rhodobacter sp) to produce CO_2 and H_2, known as the light fermentation. Combined utilization of dark and photo-fermentations was reported to improve the yield of hydrogen formation from carbohydrates [78].

Photosynthesis process: Many phototropic organisms, such as purple bacteria, green bacteria, Cyanobacteria and several algae, can be used to produce hydrogen with the aid of solar energy. Microalgae, such as green algae and Cyanobacteria, absorb light energy and generate electrons. The electrons are then transferred to ferredoxin (FD) using the solar energy absorbed by photosystem.

Biological water gas shift reaction (BWGS): The BWGS is a relatively new method for hydrogen production. Some bacteria (certain photo-heterotrophic bacteria), such as Rubrivivax gelatinosus, are capable of performing water gas shift reaction at ambient temperature and atmospheric pressure. Such bacteria can survive in the dark by using CO as the sole carbon source to generate adenosine triphosphate (ATP) coupling the oxidation of CO with the reduction of H^+ to H_2. The purple non-sulfur bacteria perform CO–water gas shift reaction in darkness, converting 100% CO into near stoichiometric amount of hydrogen.

3. Non-hydrocarbon based hydrogen production

3.1. Photodecomposition process

Lu and Li [79] carried out study on a new photocatalyst, $ZnFe_2O_4$ spinel powder in a dispersion system irradiated with visible light and under different conditions and found that the hydrogen generation rate was 0.025 ml h^{-1} (mg catalyst)$^{-1}$ in 25 ml of 0.1 M sulfide solution containing 25 mg $ZnFe_2O_4$ powder at pH 12. The dependences of H_2 production rate on pH and concentration of sulfide were also studied and it was found that $ZnFe_2O_4$ spinel powder has a good performance for H_2S photodecomposition at pH 8–12. The photocatalytic activity of $ZnFe_2O_4$ is much higher than that of ZnS–CdS under the same conditions.

3.2. Photo-electrolysis and photo-electrochemical process

Hydrogen production by photo-electrolysis involves application of heterogeneous photo-catalysts at one electrode, which is exposed to solar radiation. Additionally, the electrolysis cell is supplied with electric power at the electrodes. Due to the action of photonic radiation the required electrical energy is reduced. Photo-electrochemical cell (PEC) is a recent implementation of photo-electrolysis, which comprises photosensitive semiconductors immersed in an electrolyte and counter electrodes. The semiconductor operates similarly as a photovoltaic cell, namely it uses the photons with energy greater than the semiconductor band gap to generate electron–hole pairs that are split by the electric field which traverses the electrolyte [80].

3.3. Electrolysis and photolysis of water

Photodissociation, photolysis, or photodecomposition is a chemical reaction in which a chemical compound is broken down by photons. It is defined as the interaction of one or more photons with one target molecule. Electrolysis is a chemical process in which the current is applied to water, which is made more conductive by the addition of an electrolyte, and then the water split into hydrogen and oxygen; and hydrogen gas intensifies at the negative electrode as given by

$$H_2O \rightarrow 2H^+ + O^{2-} \tag{18}$$

In conventional electrolysis the electrolyte is contained in liquid solution, and all the energy needed to split water is supplied by electricity. Solid-polymer electrolytic (SPE) processes use solid compounds as the electrolyte rather than solutions. In high-temperature steam-electrolysis (HTSE), lower-cost heat energy, such as waste heat from cogeneration, replaces some of the electrical energy. The water is boiled, and the resultant steam is electrolyzed. Since the total energy required for splitting water is always constant, so HTSE should produce lower overall costs.

Photolysis, the splitting of water by light with the aid of (biological) photochemical electron transfer reagents analagous to chlorophyll, has been described as "the most elegant solution" to the hydrogen production problem. Unfortunately, these systems typically are very inefficient, utilizing less than 1% of the incoming energy, and thus are very costly, although recent developments suggest that improvements are possible [81,82].

If hydrogen is produced by water electrolysis, the associated emissions are those generated by the upstream electricity generation.

3.4. Water dissociation method

Lipovetsky [83] suggested that gaseous hydrogen can be produced through water dissociation process, intensified by action of a high water temperature and increase of the minus electric field, as a factor for water dissociation instead of electric current used in electrolysis. The water dissociation method makes it possible to produce concurrently both gaseous hydrogen and electric power in the operating reactor. The main power type used is thermal.

Lipovestsky [84] offered a new method for producing gaseous hydrogen, known as water dissociation method. It is based on the process of electrolytic dissociation of water with subsequent reduction of the hydrogen ions by means of the electrons, which are released during disintegration of hydroxyl ions in the plus electric field created by the hydrogen ions. The external process such as electric circuit is absent in the method of water dissociation, and this reduces considerably the specific rates of electric energy consumption as compared with water electrolysis, at the same time a number of process advantages are achieved such as abandonment of the electrolyte. All this provides for production of hydrogen whose cost should be lesser than the cost of petroleum-based fuel. Along with

hydrogen production, the method ensures the generation of electric and thermal energy. The method is clean ecologically.

3.5. Hydrogen from renewable energy sources

Ajanovic [85] worked to analyze the possible future relevance of hydrogen from renewable energy sources in the transport sector from an economic point-of-view and reported that in the transport sector a significant share of hydrogen can be expected – under very favorable conditions with respect to the development of the key parameters – at the earliest by about 2030. The major reason for this is that the costs of hydrogen and fuel cell vehicles are still very high. Only after further technological developments linked to a significant cost reduction of fuel cell vehicles and corresponding favorable political support, hydrogen from renewable energy sources could become a competitive energy carrier for transport.

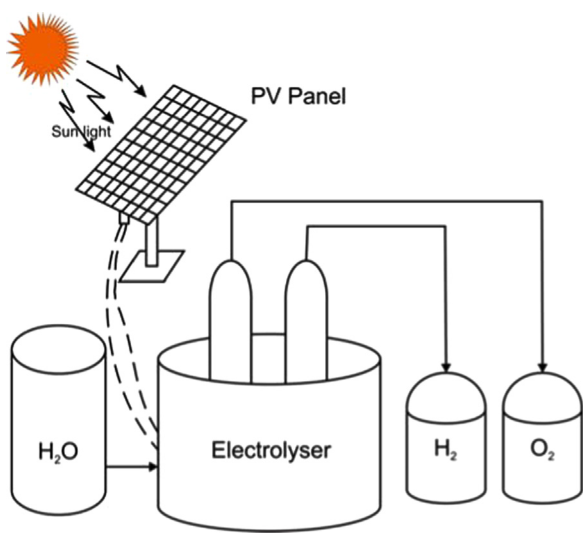


Fig. 9. Schematic diagram of photovoltaic hydrogen production system (modified after Joshi et al. [86]).

3.5.1. The photovoltaic–electrolysis system (PV–EL)

This hydrogen production system is constituted of a photovoltaic unit and a monopolar alkaline electrolysis unit. The electricity required for hydrogen production via the electrolysis unit is provided from the photovoltaic unit, which is based on electricity generation from photo-voltaic cell and subsequently electrolysis of the water, as shown in Fig. 9. The system is renewable in nature and environmentally friendly, but the rate of hydrogen production is very slow [86].

3.5.2. The wind turbine–electrolysis system (W–EL)

This hydrogen production system is a combination of a wind turbine system, which produces the necessary electricity, and a monopolar alkaline electrolysis unit. Hydrogen is produced through the electrolysis process.

3.5.3. The hydropower–electrolysis system (H–EL)

This process combines a hydropower unit and a monopolar alkaline electrolysis unit. The electrical power produced from the hydropower unit is provided to the electrolysis unit for the production of hydrogen. [87].

Out of the many processes, nearly 90% of hydrogen is produced by the reactions of natural gas or light oil fractions with steam at high temperatures (steam reforming). Coal gasification and electrolysis of water are other industrial methods for hydrogen production. These industrial methods mainly consume fossil fuel as energy source, and sometimes hydroelectricity. However, both thermochemical and electrochemical hydrogen generation processes are energy intensive and not always environment friendly. On the other hand, biological hydrogen production processes are mostly operated at ambient temperatures and pressures, thus are less energy intensive, but the hydrogen conversion efficiency is very less. These processes are not only environment friendly, but also they lead to open a new avenue for the utilization of renewable energy resources, which are inexhaustible [72].

Cetinkaya et al. [88] conducted the life cycle assessment for hydrogen production from different routes and reported that the hydrogen production capacities of wind turbines and PVs are less than the other methods. Many technologies are available for hydrogen production, but the cheapest way to produce hydrogen is natural

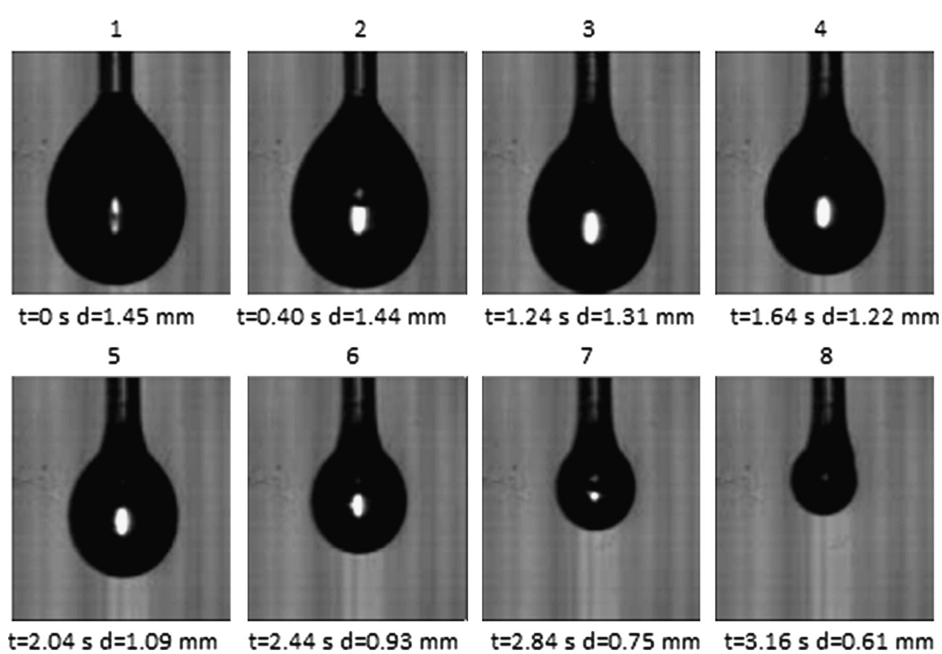


Fig. 10. Vaporization sequences of an RME droplet at 773 K and atmospheric pressure [89].

gas reforming or coal gasification at a central plant. These processes, however, produce significant amounts of CO_2 emissions. In terms of total carbon dioxide equivalent emissions, the most environmentally benign method is found to be wind electrolysis, followed by solar PV power. Large-scale hydrogen production from natural gas and coal are then environmentally affordable only if combined with carbon capture and storage technologies.

4. Properties of alternative fuels

The suitability of any alternative fuel for IC engine depends on properties of that fuel. Therefore, the required properties of alternative fuels must be characterized and identified, as per ASTM standards.

Lang et al. [43] studied about methyl, ethyl, 2-propyl and butyl esters from canola, linseed, rapseed and sunflower oils through transesterification using KOH and/or sodium alkoxides as catalysts. Chemical composition of the esters was determined by HPLC for the class of lipids and by GC for fatty acid compositions. The bio-diesel esters were characterized for their physical and fuel properties, including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion and volatility.

To characterize the mechanisms occurring in the deposit formation during the combustion of vegetable oils used as biofuels in diesel engines, it is necessary to investigate the vaporization of vegetable oil droplets under various flow, pressure and temperature conditions. Morin et al. [89] studied about the vaporization of rapeseed and sunflower oil methyl ester droplets at high temperatures; the fiber-suspended droplet technique is used and the time evolution of droplet diameter during vaporization is observed by imaging technique. The vaporization sequence is shown in Fig. 10. The droplets of vegetable oil methyl esters evaporate like mono-component droplets with a very significant heating phase.

Methyl and ethyl esters prepared from a particular vegetable oil had similar viscosities, cloud points and pour points, whereas methyl, ethyl, 2-propyl and butyl esters derived from a particular vegetable oil had similar gross heating values. However, their densities, which were 2–7% higher than those of diesel fuels, statistically decreased in the order of methyl ~2-propyl > ethyl > -butyl esters. Butyl esters showed reduced cloud points (−6 °C to 10 °C) and pour points (−13 °C to 16 °C) similar to those of summer diesel fuel having cloud and pour points of −8 °C and −15 °C, respectively. The viscosities of bio-diesels ($3.3–7.6 \times 10^{-4}$ Pa s at 40 °C) are much less than those of pure oils ($22.4–45.1 \times 10^{-4}$ Pa s at 40 °C) and were twice those of summer and winter diesel fuels (3.50 and 1.72×10^{-4} Pa-s at 40 °C), and their gross heat contents of approximately 40 MJ/kg were 11% less than those of diesel fuels (~45 MJ/kg). For different esters from the same vegetable oil, methyl esters are the most volatile, and the volatility decreased as the alkyl group grew bulkier. However, the bio-diesels are considerably less volatile than the conventional diesel fuels [43].

Sarin et al. [90] presented the fatty acid composition of different vegetable oils, as shown in Table 3. The palm oil has higher saturated fatty acids while sunflower oil has higher unsaturated fatty acids. The biodiesel oxidation stability varies with feedstock, as shown in Fig. 11.

Jatropha biodiesel, when blended with palm methyl ester, leads to a composition having efficient and improved low temperature property as well as good oxidation stability. The feedstock for the synthesis of biodiesel must have a suitable combination of saturated as well as unsaturated fatty compounds to achieve improved oxidation stability and low temperature properties. Jatropha biodiesel has poor oxidation stability with good low temperature properties. On the other hand, Palm biodiesel has good oxidative stability, but poor low temperature properties. The combinations of Jatropha and Palm give an additive effect on these two critical properties of biodiesel. The stability of biodiesel is very critical and biodiesel requires antioxidant to meet storage requirements and to ensure fuel quality at all points along the distribution chain. In order to meet EN 14112 specification, 200 ppm concentration of antioxidant is required for biodiesel (except palm biodiesel), which is much higher than that required for petroleum diesel. In order to minimize the dosage of antioxidant, appropriate blends of Jatropha and palm biodiesel are made. It was found that antioxidant dosage could be reduced by 80–90%, if Palm oil biodiesel is blended with Jatropha biodiesel at around 20–40% concentration.

Since palm biodiesel has poor low temperature properties like cloud point and pour point, the blending of Jatropha biodiesel improves the same. Therefore, optimum mixture of Jatropha

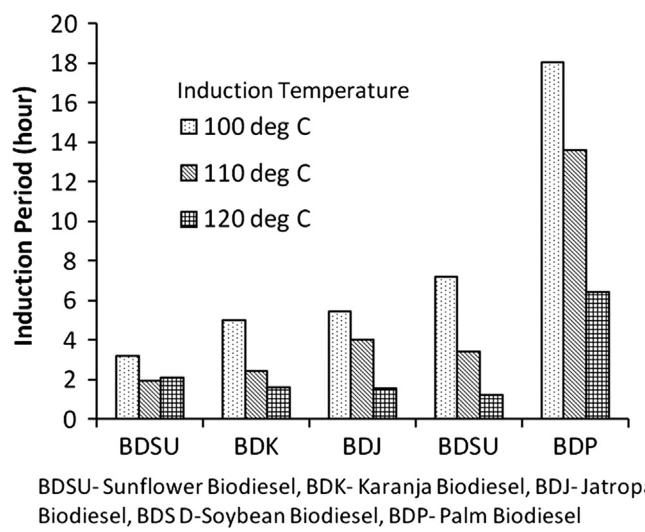


Fig. 11. Biodiesel oxidation stability variation with feedstock.

Table 3
Fatty acid composition of different vegetable oils [90].

Fatty acid	Jatropha Oil	Pongamia (Karanjia) Oil	Sunflower oil	Soyanbean oil	Palm oil
Lauric ($C_{12}/0$)	–	–	0.5	–	–
Myristic ($C_{14}/0$)	–	–	0.2	0.1	–
Palmitic ($C_{16}/0$)	14.2	9.8	4.8	11.0	40.3
Palmitoleic ($C_{16}/1$)	1.4	–	0.8	0.1	–
Stearic ($C_{18}/0$)	6.9	6.2	5.7	4.0	3.1
Oleic ($C_{18}/1$)	43.1	72.2	20.6	23.4	43.4
Linoleic ($C_{18}/2$)	34.4	11.8	66.2	53.2	13.2
Linoleic ($C_{18}/3$)	–	–	0.8	7.8	–
Archidic ($C_{20}/0$)	–	–	0.4	0.3	–
Behinic ($C_{22}/0$)	–	–	–	0.1	–
Saturates	21.1	16.0	11.6	15.5	43.4
Unsaturates	78.9	84.0	88.4	84.5	56.6

biodiesel with palm biodiesel can lead to a synergistic combination with improved oxidation stability and low temperature property [90].

Dimethyl ether (chemical structural formula CH_3–O–CH_3) is one of the simplest ether compounds. Its physical and chemical properties compared with diesel are low heat value of DME which is only 64.7% of that of diesel. The cetane number of DME is higher and the auto-ignition temperature is lower than those of diesel; the latent heat of evaporation of DME is much higher than that of diesel [91].

The operation of a DME engine requires a new storage system and a new fuel delivery system. The engine itself does not need modification, however, in order to achieve an equivalent driving range as that of a CIDI diesel, a DME fuel storage tank must be twice the size of a conventional diesel fuel tank due to the lower energy density of DME compared with diesel fuel. The most challenging aspects of a DME engines are related to its physical properties and not to its combustion characteristics. The viscosity of DME is lower than that of diesel by a factor of about 20, causing an increased amount of leakage in pumps and fuel injectors. There are also lubrication issues with DME, resulting in premature wear and eventual failure of pumps and fuel injectors [21].

Lang et al. [43] worked on monitoring of transesterification reaction, identified and quantified seven types of fatty acids in the vegetable oil esters based on GC analysis, and all these esters were about 90% unsaturated. The esters made from different vegetable oils had a unique dominant fatty acid compound. The difference in fatty acid composition apparently affected various fuel properties of the esters such as viscosity and pour point. The physical and fuel properties of ethyl esters in general were comparable to those of methyl ester from the same oil. The two butyl esters showed improved cold flow properties than both their methyl and ethyl counterparts. The heat of combustion of the vegetable oil esters was approximately 40 MJ/kg. Since the esters were denser, the energy content of a full tank of biodiesel fuel would be only 4–9% less than the diesel fuel.

The esters were found to be considerably less volatile than the diesel fuels. Some residue was left from biodiesels at 350 °C, which could cause coke deposit on injectors in engines. Biodiesels made from different vegetable oils and alcohols have some of the properties at par with the conventional diesels, but have higher viscosity, which is a limiting factor for utilization of neat biodiesels in the compression ignition engines. Therefore, biodiesel blends can be used in diesel engines, to trade off the economic condition and the emissions. Some anti-gelling additives may be needed to improve the cold flow property if bio-diesels are used under severe winter conditions.

Bio-oils are biomass products, carbon neutral in life cycle term and renewable in nature. But these have higher moisture contents, higher viscosity and lower calorific value as compared to the diesel. Table 4 shows the physical and chemical properties of various bio-oils.

4.1. Emission characteristics of alternative fuels

Due to the increasing interest in the use of biodiesel, the Environmental Protection Agency, USA, conducted a comprehensive analysis of the emission impacts of biodiesel using publicly available data. This investigation made use of statistical regression analysis to correlate the concentration of biodiesel in conventional diesel fuel with changes in regulated and unregulated pollutants [99]. The average effects of percent biodiesl on NOx and CO emissions are shown in Fig. 12.

Salvi and Jindal [100] carried out the study on performance and emissions characteristics of direct injection diesel engine fueled with linseed oil biodiesel blends and diesel fuel at different blends. It was concluded that with 10% linseed biodiesel blend (LB10), better thermal efficiency (8–11%) and lower specific fuel consumption (3.5–6%), decreased CO, smoke and hydrocarbon emission were the advantages. On the contrary, a little increase in NOx emission was confronted. With the advantages, linseed proves to be a potential source for deriving alternative and renewable fuel for internal combustion engines. Since, linseed biodiesel is renewable in nature, so practically negligible CO_2 is added to the environment.

At SPRERI holistic approach was taken to utilize all components of the Jatropha fruit—shell for combustion, hull/husk for gasification, oil and bio-diesel for running compression ignition engines, cake for production of biogas and spent slurry as manure and it has been found that all components of the Jatropha curcas fruit can be utilized efficiently for energy purposes [101].

Huang et al. [91] studied the combustion characteristics of a light-duty direct-injection diesel engine operating on dimethyl ether (DME). The indicated pressure diagrams and injector needle lifts are recorded, and the combustion characteristics are demonstrated and compared with those of an engine operated on diesel fuel. The experimental and calculated results show that the DME fueled engine has a longer delay of injection and duration of injection, a lower maximum cylinder pressure and rate of pressure rise, as well as a shorter ignition delay as compared with those of a

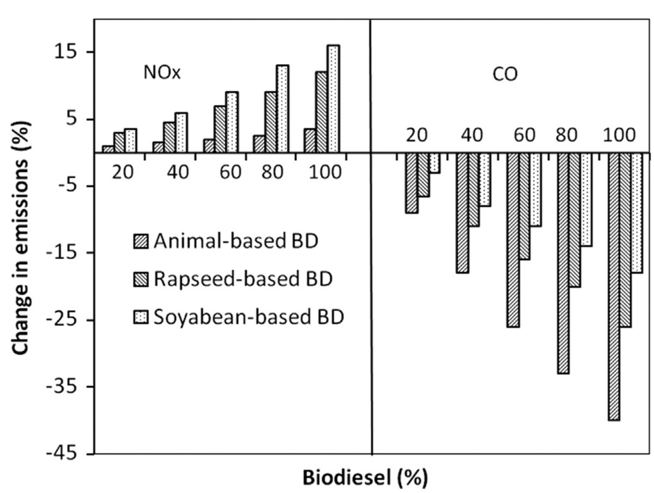


Fig. 12. Effects of biodiesel sources on NOx and CO emissions [99].

Table 4
Physical and chemical properties of bio-oil.

Bio-oil	Moisture (wt%)	pH	Density at 24 °C (kg/m^3)	Viscosity at 50 °C (mm^2/s)	LHV (MJ/kg)	C (wt%)	H (wt%)	O (wt%)	N (wt%)	S (wt%)	Reference
Palm shell	53	2.5	1051	3.2	10	19.48	8.92	71.40	0.2	0.04	[63]
Rice husk	25.2	2.8	1190	128	17.42	41.7	7.7	50.3	0.3	0.2	[92]
Cotton stall	24.4	3.3	1160	125	17.77	42.3	7.9	42.3	0.3	0.2	[93]
Sugar cane trash	52.14	3	1019.20	2.31	15.48	–	–	–	–	–	[94]
Softwood	13.0	3.0	1188 (at 28 °C)	–	27.9	62.3	7.00	-	1.1	0.07	[95]
Softwood	5.3	–	1051(at 40 °C)	24	32.4	77.56	8.69	13.3	0.59	–	[96]
Soybean	0.001	3.82	993	62 (40 °C)	–	–	–	–	–	–	[97]
Linseed	21.5		4.0	58 (40 °C)	–	–	–	–	–	–	[98]

diesel engine. The engine with DME fuel has a low mechanical load and combustion noise, a fast rate of diffusion combustion and shorter combustion duration than that of a diesel engine.

Using biodiesel instead of conventional diesel fuel reduces emissions such as the overall life cycle of carbon dioxide (CO_2), particulate matter, carbon monoxide, sulfur oxides (SOx), volatile organic compounds (VOCs), and unburned hydrocarbons significantly. However, biodiesel fueled diesel engine increases nitrogen oxides (NOx) emissions, mostly NO and NO_2, which are considered as zone-A hazardous compounds. It is becoming more important to study the feasibility of substitution of diesel with an alternative fuel, which can be produced locally on a substantial scale for commercial utilization. The biodiesels derived from vegetable oils are considered as good alternatives to diesel as their properties are close to diesel [4,102].

5. Conclusions

The search for alternative fuels has been vitally important for quite some time. A variety of methods and technologies are currently available for the production of alternative fuels, which can be classified in different ways. Among the various technologies esterification and gas-to-liquid are the most useful.

Biodiesel fuels are primarily the methyl/ethyl esters of fatty acids derived from a variety of vegetable oils and animal fats. Biodiesel is completely miscible with petroleum diesel fuel, and is generally tested as a blend. The major obstacle to the widespread use of biodiesel is its high cost relative to petroleum.

The production of biodiesel from microalgae may be a viable alternative fuel in the future, but greater technological advancement and ecological study is still required in order to make this feasible.

In order to make the GTL technology more viable and cost-effective, attention must be given to reducing both the capital and the operating costs. Further improvements regarding to the activity and selectivity of the Fischer–Tropsch catalyst can also yield a significant reduction in the operating cost of such a plant.

The hydrogen fuel is a carbon free energy carrier and that can be produced from the renewable energy sources. There are many technologies available for hydrogen production, but economical viability in terms of production, storage and safety are still some of the hurdles for the full utilization of hydrogen as an alternative fuel. In future, the increasing price, depletion of petroleum based fuels and environmental concern may force the hydrogen fuel economy.

While developing alternative fuel for transportation vehicles, mainly engine constraints, economic and environmental issues must be considered for creating viable and sustainable fuel. Although many resources and technologies are already available, still more resources have to be explored and subsequently production technologies have to be upgraded in order to meet the fuel quality requirement of IC engines.

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